

REMARKS

In view of the above amendments and following remarks, reconsideration and further examination are requested.

In reply to the objection to claim 22, this claim has been amended so as to depend from claim 18. In reply to the 35 U.S.C. 112, second paragraph, rejection of claim 24, this claim has been amended to include the term --1%-- at the end thereof. Claims 13, 14, 17, 21, 23, 25, 27 and 30-32 have been amended so as to more clearly bring out an inventive feature of the invention. And, claim 33 has been added.

In the Final Rejection mailed April 4, 2007, claims 17-26 were rejected under 35 U.S.C. 102(b) as being anticipated by EP '347. This rejection is respectfully traversed for the following reasons.

In supporting the rejection of claims 17-26, the Examiner has taken the position that the heating and pulling of the reinforcing material 23 as expressed in paragraph [0033] of EP '347 will indeed stretch the reinforcing material. However, it is respectfully submitted that there is nothing in EP '347 to indicate that the heating and pulling discussed therein will necessarily result in any stretching of the reinforcing material 23. In this regard, there is nothing in EP '347 to suggest that a sufficient tension is created by this heating and pulling to indeed stretch reinforcing material 23. Accordingly, absent any explicit disclosure in EP '347 that reinforcing material 23 is indeed stretched, and absent any disclosure of any specific parameters that will indeed result in stretching of the reinforcing material upon the heating and pulling thereof, it does not necessarily flow from EP '347 that reinforcing material 23 is stretched as proffered by the Examiner. Thus, for this reason alone claim 17 is not anticipated by EP '347.

Additionally, claim 17 also requires that the synthetic resin of the tape and the thermoplastic resin of the fibrous member are *in the same family*. Because the fiber-forming resin and the tape-forming resin of the instant invention are in the same family, an adhesive force is developed between the fiber and the tape to allow for full realization of the reinforcing function performed by the stretched fibrous member. EP '347 is silent with regard to the synthetic resin of reinforcing material 23 and the material of belt member 21 being in the same family. Accordingly, for this additional reason, claim 17 is not anticipated by EP '347.

"Stretching" (or "orientation") is an operation exercised in the field of resin processing by, for example, applying a force of tension to a resin filament at a temperature which is below the melting point and above the glass transition temperature of the resin, to increase a length of the filament several times. As a result, this stretched resin filament is provided with an enhanced orientation (i.e. an enhanced orientation of molecular chains forming the filament). In accordance with the instant invention, such stretching results in a filament exhibiting a far superior tensile strength (470 MPa as expressed at page 17, line 2, of the original specification, for example) as compared to a filament that is not stretched (tensile strength of 65 – 70 MPa as expressed at page 18, lines 6–8, of the original specification).

For a better understanding of the "stretching" referred to above, provided herewith are copies of the following two references.

- 1) Encyclopedia of Polymer Science and Engineering, Vol. 2, pp. 454 – 459
(please see page 455), and
- 2) Encyclopedia of Polymer Science and Engineering, Vol. 12, pp. 234 – 241
(please see page 239).

In contrast to the above, "extrusion molding" referred to in paragraph [0033] of EP '347 is an operation of extruding a resin at a temperature above the melting point of the resin to form the resin into an elongated shape. Accordingly, if a resin of the same family as the molten resin forming the belt member 21 is used as the reinforcing material 23, as asserted by the Examiner, then based on [0034] of EP '347, this reinforcing resin member will be melted together with the belt-forming resin in mandrel 7 so as to lose its reinforcing function. And, in such a melted state, the reinforcing material 23 fails to receive sufficient tension necessary for causing molecular orientation. Thus, based on the method employed by EP '347, the reinforcing material 23 is not in the same family as the material of belt member 21, the reinforcing material 23 is not stretched, or both.

Irrespective of the above, to more clearly bring out an inventive feature of the invention, claim 17 has been amended to recite that the fibrous material is --stretch-oriented-- as opposed to being "stretched". Support for this amendment is believed to be found on page 12, lines 3-9 of

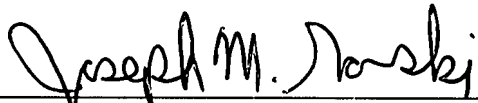
the original specification, for example. EP '347 is silent with regard to any orientation of the reinforcing material 23 resulting from performing the method of EP '347.

In view of the above amendments and remarks, it is respectfully submitted that the present application is in condition for allowance and an early Notice of Allowance is earnestly solicited.

If after reviewing this Amendment, the Examiner believes that any issues remain which must be resolved before the application can be passed to issue, the Examiner is invited to contact the Applicants' undersigned representative by telephone to resolve such issues.

Respectfully submitted,

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July 9, 2007

ENCYCLOPEDIA OF POLYMER SCIENCE AND ENGINEERING

VOLUME 2

**Anionic Polymerization
to
Cationic Polymerization**

A WILEY-INTERSCIENCE PUBLICATION

John Wiley & Sons

NEW YORK • CHICHESTER • BRISBANE • TORONTO • SINGAPORE

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**Library of Congress Cataloging in Publication Data:
Main entry under title:**

Encyclopedia of polymer science and engineering.

Rev. ed. of: Encyclopedia of polymer science and technology. 1964—

"A Wiley-Interscience publication."

Includes bibliographies.

I. Polymers and polymerization—Dictionaries.

I. Mark, H. F. (Herman Francis), 1895—

II. Kroschwitz, Jacqueline I. III. Encyclopedia of polymer science and technology.

TP1087.E46 1985 668.9 84-19713

ISBN 0-471-88786-2 (v. 2)

Printed in the United States of America

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of extrusion, this process is more suitable for polyolefin and other heat-stable materials.

A modification is the reciprocating-screw method used for bottles between 250 mL and 10 L in volume. After the parison is extruded, the screw moves back, accumulating melt in front of its tip. When the previously molded bottle has cooled, the mold opens, the bottle is removed, and the screw quickly moves forward, pushing plastic melt through the extrusion head forming the next parison; up to twelve parisons can be extruded simultaneously. A reciprocating-screw extrusion blow molder for a dairy bottle is shown in Figure 10.

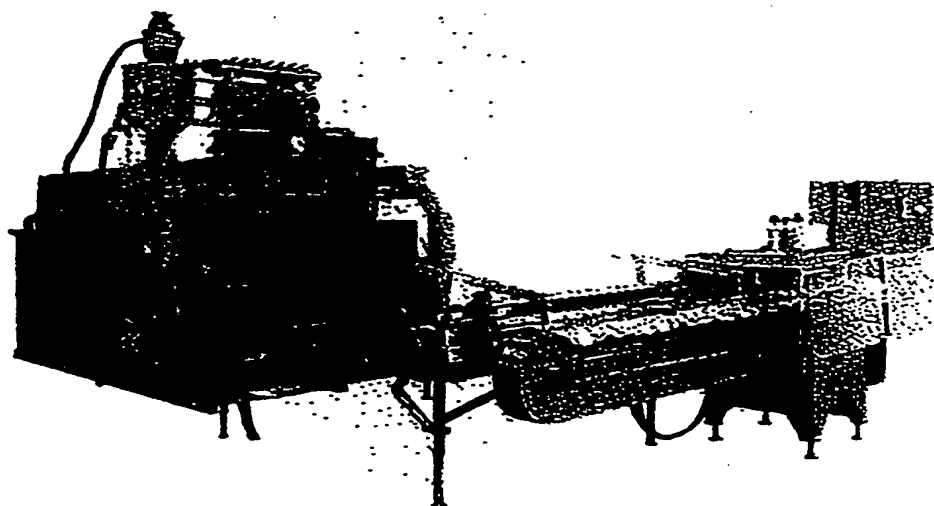


Fig. 10. Uniloy 350R2 8-head intermittent extrusion blow molder for the manufacture of 2-L ($\frac{1}{2}$ -gal) milk bottles with handles. Production rates of over 65 bottles per minute have been achieved; also shown is the flash trimmer. Courtesy of Hoover Universal, Inc.

Another modification is the ram-accumulator method, although no longer in widespread use. It is intended for parts weighing 2 kg or more. This system, much like the reciprocating-screw method, is used to extrude quickly heavy parisons that might sag or be deformed by their own weight. The accumulator is a reservoir mounted alongside the extruder. A piston or plunger pushes the melt through the extrusion head. In this method, unlike in the reciprocating-screw process, melt that enters the reservoir first is last to leave. As a result, melt history of the resin is not uniform.

The accumulator head (see Fig. 11) has replaced the ram accumulator in its application for heavy parts. The tubular reservoir is a part of the extrusion head itself. Plastic melt that enters the head first is first to leave. A tubular plunger quickly extrudes the melt from the head annulus with a low, uniform pressure, which helps reduce the stresses found in other systems.

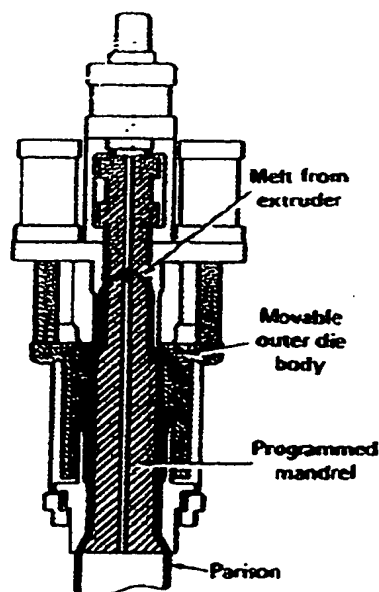


Fig. 11. Typical accumulator head.

Related to extrusion blow molding is the extrusion-molded neck process (see Fig. 12). Still used by Owens-Illinois, this proprietary process can be traced to glass-blowing technology. In an unusual approach, the bottle neck is injection-molded and the bottle body is extrusion blow-molded. The two halves of the neck-finish cavity or neck ring are mounted to an actuating-head assembly, which intermeshes with the two halves of the blow-mold cavity. The process cycle begins with the main-body mold cavity open and the neck-ring cavity closed. The actuating-head assembly moves downward to contact the extrusion die head. When in position, extrusion pressure fills the neck section with plastic melt. After holding for one to two seconds, the head assembly moves upward while the parison is extruded. When the head assembly reaches the top of its stroke, the blow-mold cavity closes on the parison. The remaining steps of flash pinch-off, blowing, and part removal follow conventional techniques. Although the production cycle is somewhat slow, the process offers the advantages of an accurately molded neck and of a parison held at both ends.

Stretch Blow Molding. For stretch blow molding, mainly poly(ethylene terephthalate), poly(vinyl chloride), polypropylene, and polyacrylonitrile are used (3,6). In this process, based on the crystallization behavior of the resin, a parison or preform is temperature-conditioned and then rapidly stretched and cooled. For best results, the resin must be conditioned, stretched, and oriented just above the glass-transition temperature. At this point, the resin can be moved without the risk of crystallization (see Figs. 13 and 14).

This process improves product performance, such as bottle-impact strength, cold strength, transparency, surface gloss, stiffness, and gas barrier (3,6). The bottles are lighter and less costly, and products that otherwise would not be suitable can be packaged. The process uses injection-molded, extruded, or extrusion blow-molded parisons in one or two steps.

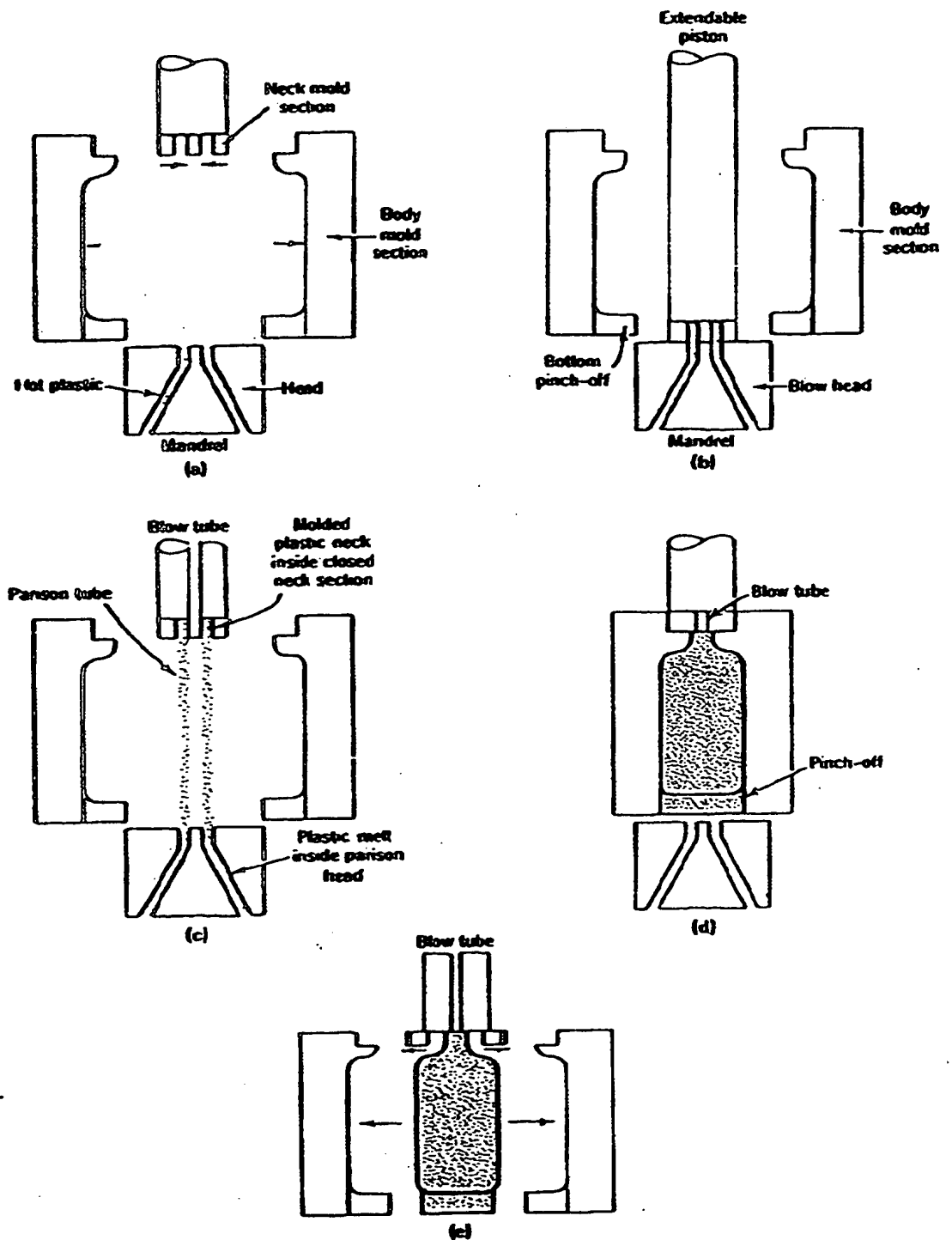


Fig. 12. Extrusion-molded neck blow-molding process. (a) Body section open, neck section closed, neck section retracted; (b) neck section extended to mate with parison nozzle (plastic fills neck section); (c) neck section retracted with parison tube attached; (d) body section closed, making pinch-off (parison blown to body sidewalls); (e) body molds open, neck molds open, bottle about to be ejected.

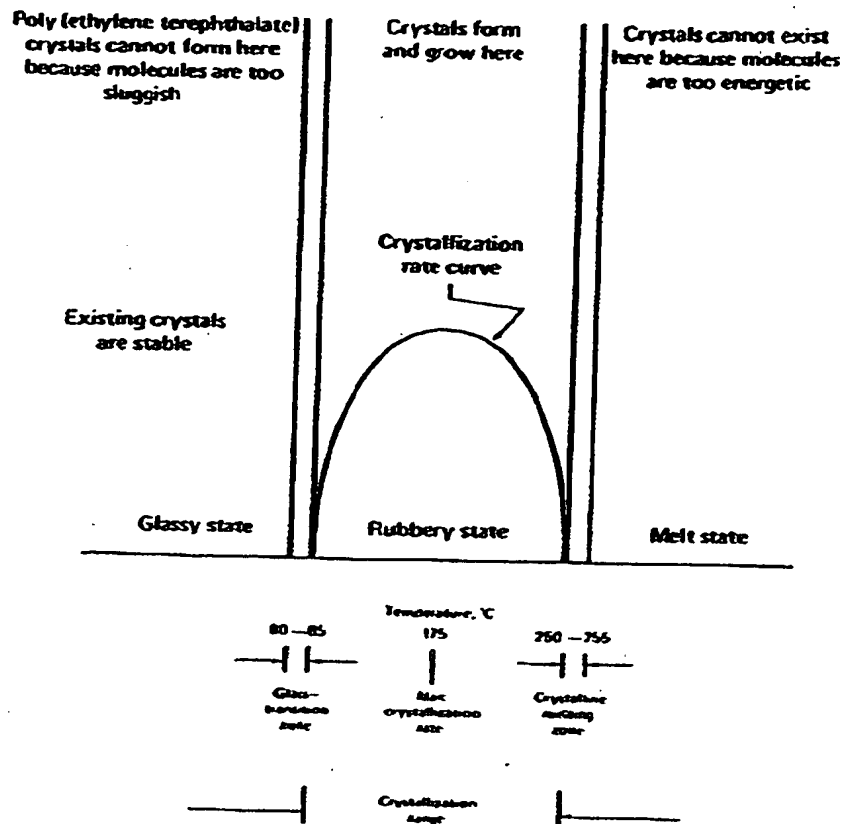


Fig. 13. Molders' diagram of crystallization behavior (8). Courtesy of the Society of Plastics Engineers.

In the one-step method, parison production, stretching, and blowing take place in the same machine. In the two-step method, the parison is produced separately from stretching and blowing. The main advantage of the one-step approach is the savings in energy. The parison is rapidly cooled to the stretch

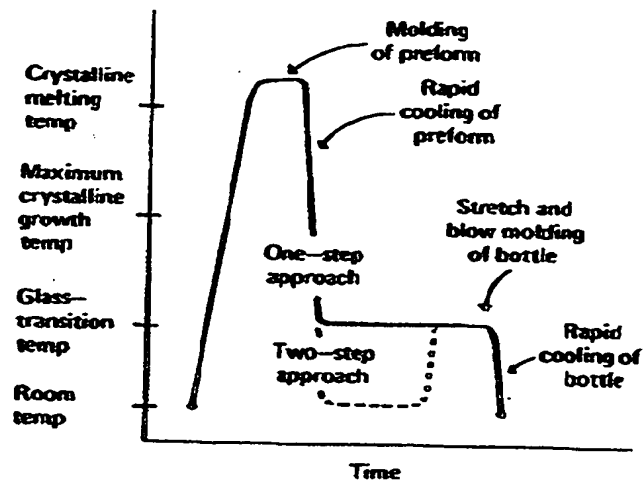


Fig. 14. Basic stretch blow process. Courtesy of Jerome S. Schaul.

temperature. In the two-step approach, the parison is cooled to room temperature and reheated to the stretch temperature (see Fig. 14). On the other hand, production in the two-step method is more efficient, and a minor breakdown in one of the steps does not stop the other. The optimum balance of design vs output is also easier to achieve with the two-step approach. Limits on parison production, for example, do not force a compromise in parison design to achieve higher bottle production. For optimum performance, each bottle design has a unique parison-design and temperature-conditioning requirement which may or may not fit, for optimum productivity, the assumptions used in the design of the one-step equipment.

In the injection stretch blow process, the parison is virtually the same as that used in injection blow molding. Both one- and two-step methods are used. In the two-step method, the parison is injection-molded in a separate machine, sorted, and placed in an oven for temperature conditioning and blow molding. A rod is used inside the parison, in combination with high air pressure, to complete the stretch (see Fig. 15). Injection stretch blow molding is commonly used for poly(ethylene terephthalate) resin.

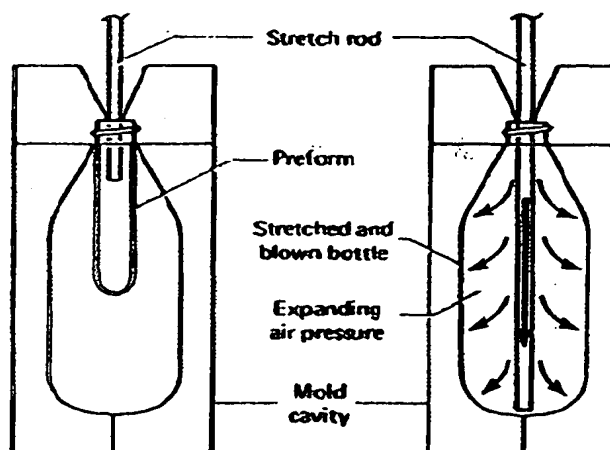


Fig. 15. A temperature-conditioned preform is inserted into the blow-mold cavity and is rapidly stretched. A rod is often used to stretch the preform in the axial direction, and air pressure to stretch the preform in the radial direction.

The extruded parison stretch process can use either the one- or two-step method. In the former, a tube is extruded and fed directly into an oven for conditioning. After conditioning, the tube is cut into parison lengths. Mechanical fingers grab both ends and stretch the parison. The two mold halves close, whereupon air pressure expands the stretched parison against the mold cavity. In the two-step method, the extruded tube is cooled and cut to length. Later, the cut tubes are placed in an oven for conditioning. This technique is used mainly for polypropylene, and occasionally for poly(vinyl chloride).

With the extrusion blow stretch process, the parison is shaped and temperature-conditioned in a preform cavity in the same way a bottle is extrusion blow-molded. From this preform cavity, the parison is transferred to the bottle cavity, where a rod and air pressure combine to stretch and expand the resin. Poly(vinyl

chloride) is most often stretch blow-molded with this process. Although the one-step method is the most common (see Fig. 16), a two-step technique, in the same fashion as the others, is feasible.

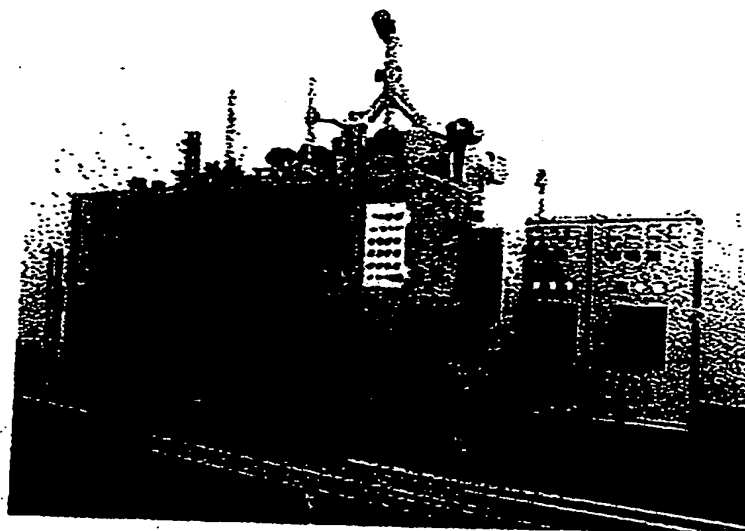


Fig. 16. Bekum BM04D continuous extrusion blow molder for the manufacture of biaxially oriented poly(vinyl chloride) bottles. Production rate for 1-L bottle is 2000 per hour; maximum bottle size is 2 L. Courtesy of Bekum Plastic Machinery, Inc.

Multilayer Blow Molding. All materials, whether metal, glass, or paper, have certain strengths and weaknesses, and advantages and disadvantages. Frequently, two or more materials can be layered and combined, eg, chromium-plated steel, laminated automobile windshields, and wax- or polyethylene-covered paperboard. In multilayer blow molding, the advantages of two or more resins are combined to produce packaging superior to that produced by a single resin (see also FILMS, MULTILAYER; SHEET-MOLDING COMPOUNDS).

Bottles must be strong, clear, inexpensive, compatible with other products, and provide a gas barrier. Low-cost polyethylene and polypropylene, for example, are approved for food contact, and are excellent barriers to water vapor, though not to oxygen. As such, they are not suited for packaging oxygen-sensitive foods requiring long shelf life. Poly(ethylene-co-vinyl alcohol), on the other hand, is a relatively expensive material which provides an excellent barrier, but it is sensitive to water, which can affect its properties. A thin layer sandwiched between two layers of polyethylene or polypropylene can solve this problem.

All basic blow-molding methods are used in multilayer blow molding. Plasticizers or extruders are generally added to each resin. The continuous coextrusion process is used for bottles up to 5 L in size, whereas the accumulator-head process is used for drums and tanks up to 500 L in size. The coinjection process is used for small bottles 500 L in size.

Related to the coinjection process is a thermoform-insert process (9). A coextruded sheet is thermoformed into an insert, which is placed on the core rod of

ENCYCLOPEDIA OF POLYMER SCIENCE AND ENGINEERING

VOLUME 12

**Polyesters
to
Polypeptide Synthesis**

A WILEY-INTERSCIENCE PUBLICATION

John Wiley & Sons

NEW YORK • CHICHESTER • BRISBANE • TORONTO • SINGAPORE

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Library of Congress Cataloging in Publication Data
Main entry under title:

Encyclopedia of polymer science and engineering.

Rev. ed. of: Encyclopedia of polymer science and technology. 1964—

"A Wiley-Interscience publication."

Includes bibliographies.

I. Polymers and polymerization—Dictionaries.

I. Mark, H. F. (Herman Francis), 1895—

II. Kreschwitz, Jacqueline I. III. Encyclopedia of polymer science and technology.

TP1087.E45 1985 668.9 84-19713
ISBN 0-471-80944-6 (v. 12)

Printed in the United States of America

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coupled with good arc resistance and dielectric strength. Underwriters' Laboratory has endorsed the exceptional stability of these resins for electrical and mechanical properties by assigning continuous-use temperature ratings ranging from 105 to 140°C. Many PBT grades have UL ratings allowing them to be used in class B (130°C) and class F (155°C) electrical-insulation systems. PET's outstanding recognition also includes approval for class H (180°C) systems. Typical electrical-property ranges are dielectric strength, 14–25 kV/mm; dielectric constant (1 kHz), 3.1–3.8; volume resistivity, 10^{16} Ω -cm; and dissipation factor (1 kHz), 0.001. Compounds are available with zero arc-tracking resistance under high voltage per UL Bulletin 746A.

Weathering. In general, TPE resins have limited weather resistance, which can be made acceptable by adding stabilizers. Figure 4 shows the drop in PBT impact strength as a function of exposure time in a carbon arc WeatherOmeter (138) for both black and uncolored resins. Pigmented products, primarily black, are recommended for improved outdoor stability. Polymer degradation from uv exposure, particularly in the presence of heat, moisture, oxygen, or atmospheric pollutants, can result in embrittlement, chalking, surface crazing, discoloration, and loss of physical properties such as strength and impact (142). Stabilization of TPE materials against weathering damage can be achieved by adding uv-screening agents, absorbers, and quenchers.

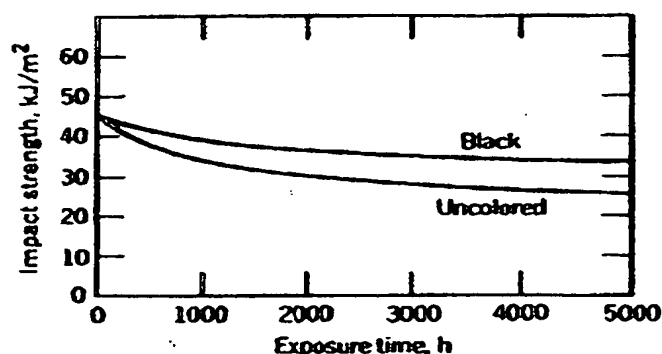


Fig. 4. The effect of uv exposure on impact strength of PBT reinforced with 30 wt % glass fiber with black and uncolored resins (138). To convert kJ/m² to ft-lbf/in.², divide by 2.10.

Processing

An important attribute of TPEs is their ability to be processed easily to yield a wide variety of molded parts, extruded shapes, sheeting, film, monofilament, or fibers.

Injection Molding. PBT and PCTI (Kodak A-150) have been used successfully for nearly 15 years as injection-moldable crystalline and amorphous thermoplastics, respectively. Unmodified PET had not been acceptable as an injection-molding resin because it crystallizes slowly and needs a mold temperature of 130–140°C. A number of modified PET resins that crystallize faster and are processed at mold temperatures below 100°C have been developed (143).

Before processing any TPE, drying is very critical to avoid hydrolysis during processing, which can cause a lower molecular weight and loss of mechanical properties (143,144). Commercially supplied PET resins can have a moisture content up to 400 ppm; during processing hydrolysis can occur at a moisture level above 200 ppm. Therefore, it is always recommended to dry the resins to a moisture content <200 ppm and maintain this level. In comparison to PET, PBT is less susceptible to hydrolysis and 400 ppm is the maximum recommended moisture content (145). Usual drying conditions for PBT are 2–4 h at 125°C; 3–5 h at 135–150°C is recommended for PET.

Injection molding of PBT (145–148), PET (149–152), and PCTI (153) can be done on plunger, preplasticating screw plunger, or reciprocating screw-ram, injection-molding machines. It is recommended that barrel temperatures should be maintained at the lowest level to minimize melt degradation, which occurs at 240°C for PBT and at 290°C for PET. The preplasticating screw plunger and reciprocating screw-ram machines are preferred because they homogenize the melt at lower temperatures than the plunger machine and thus allow lower barrel temperatures and more rapid cycles. The machine should be sized so that the shot volume does not exceed 80–85% of the barrel capacity. Conventional molding machines for TPEs have a general-purpose screw design (qv) with a length-to-diameter ratio ($L:D$) of up to 18–24:1 (145). It is necessary to use a nozzle heater to prevent freezing of the rapidly crystallizing polymers, especially PBT. It is also recommended to use a shut-off nozzle with a minimum orifice diameter of 5 mm to eliminate drooling of the low viscosity melt.

The recommended processing conditions for TPEs are given in Table 4. The key processing variables that affect molding and part performance are the moisture level of the melt during processing, mold temperature, wall thickness, and the interaction of wall thickness with mold temperature. These are by no means the only important variables, but they are critical in establishing part quality and molding conditions. Extensive processing observations from laboratory investigations and field trials, along with analytical measurements, have substantiated the influence of these variables on modified PET molding and finished part performance (114).

Special attention should be placed on the processing temperatures used to injection-mold TPEs. Typically, unreinforced and glass-reinforced PBT should be processed at a cylinder temperature of 240–260°C and at high injection speeds; the upper temperature limit is reduced to 250°C for flame-retardant formulations. The major aim should be to keep the melt residence time in the cylinder to a minimum. This also means that the ratio of shot capacity (machine or cylinder size) to the weight of the part should not exceed 2:1. Special care is necessary when hot runners are used for molds. It is also recommended that the actual temperature of the melt should be monitored as it emerges through the nozzle, and the temperature controller should be adjusted accordingly, as the difference between the two values may be considerable. The principal PET grades are reinforced either with glass fiber or glass-mineral combinations. Within these types of resins, there are impact-modified, flame-retarded, and other specialty grades. Melt temperatures generally are 260–270°C, with flame-retarded grades having an upper melt-temperature limit of 295°C.

All PBT grades have high solidification and crystallization rates, which

Table 4. Injection-molding Conditions Recommended for Thermoplastic Polyesters^a

Grade	Melt-temp range, °C	Injection pressure, MPa ^b	Injection speed	Mold temp, °C	Gating dia, mm ^c	Shrinkage range, %	Minimum time, s ^d
PBT							
unmodified resin	345-355	46	medium-to-fast	90-120	1.3	1.8-2.2	35-50
reinforced resin ^e , 20-30 wt %	250-265	55	fast	80-80	1.6	0.7-1.2	30-45
Impact-modified, unfilled or filled	230-250	48	fast	85-90	2.4	1.7-2.2	50-100
PET							
unmodified resin	260-270	46	medium-to-fast	82-120	0.5-2.5	2.0	40-60
reinforced resin ^e , 15-55 wt %	270-310	55	medium-to-fast	82-120	0.5-2.5	0.2-0.6	15-18
Impact-modified, 30-35 wt % reinforced	275-300	55	fast	85-120	0.5-2.5	0.2-0.9	16-18
PCTI							
unmodified resins	230	80	fast	25-50	1.5	0.1-0.4	20-40

^a Refs. 3, 154, and 155.

^b To convert MPa to psi, multiply by 145.

^c Data based on 3.2-mm wall thickness.

^d Glass, mineral, mineral-glass, all with or without flame retardants.

permit rapid processing and short production cycles. Thus fast injection speeds have to be selected to avoid cooling and solidification of the melt during the mold filling. Care must be taken at high injection speeds to ensure that the mold is well vented, since excess compressed air may cause burn marks. Good melt flow, in conjunction with appropriate injection- and molding-pressure settings, results in faithful reproduction of mold contours. PET grades also have fast crystallization rates and their processing speeds are almost as high as for PBT. For both PET and PBT the injection and clamping pressures should always be high. Good results are obtained with injection pressures of 10–60 MPa (1450–8700 psi) and screw speeds of 40–70 rpm.

As a result of the high crystallinity of PBT and PET, mold shrinkage is high. Fiber-reinforced grades exhibit anisotropic mold shrinkage which leads to warpage in large parts. The shrinkage of 30 wt % glass-reinforced PBT in the flow direction is 0.4–0.6%; in the transverse direction, the value is larger, 0.8–1.0% resulting from differences in fiber orientation (138). Shrinkage as high as 1.7–2.3% may occur in heavy sections. Shrinkage of PET parts may be slightly less. There are appreciable differences in mold shrinkage between nonreinforced and filled resins. Virgin grades have essentially the same shrinkage in the flow and transverse directions. The individual processing parameters influencing shrinkage must be controlled carefully. Mold temperature and wall thickness of the part also have considerable influence on mold- and postshrinkage. The mold temperature also affects the translucency of moldings caused by differences in crystallinity. With increased mold temperature, the color of the parts may be paler due to lower crystallinity. For this reason, recommended mold temperatures are 80–90°C and 80–120°C for PBT and PET, respectively. Gate designs should be sufficiently large in cross section to permit long dwell times. The type and location of the gate should always be chosen to give a uniform flow front and linear filling of the mold cavity. In all grades wall thicknesses and mold temperatures should be as uniform as possible. Another possible way of influencing warpage is to set different temperatures in the two halves of the mold. The effect of this temperature difference on nonreinforced PBT is comparatively large. In glass-reinforced grades it is possible to influence warpage only if the temperature differences are extreme. The shrinkage differential parallel and perpendicular to the flow direction can be reduced by using mixtures of glass fiber and spheres.

PBT is suitable for the manufacture of close-tolerance precision articles. However, the production of such moldings with high dimensional fidelity in nonreinforced PBT requires a mold temperature of 120–140°C, giving completely crystallized parts. This processing temperature prevents postshrinkage caused by postcrystallization and maintains dimensional stability when parts are later subjected to high service temperatures. On the other hand, mold temperatures for precision articles of glass fiber-reinforced PBT can be 80–90°C and subsequent annealing (qv) is not required. The molding of metal or other inserts presents no problems with TPEs under normal processing conditions (138) (see also INJECTION MOLDING).

Extrusion. The TPEs are easily extruded into a number of configurations, ie, film, sheeting, tubing or pipe, profile, and monofilament (153,156–159). Satisfactory extrusion can be achieved with extruders capable of heating the melt to 250–300°C and having *L:D* ratios of 20:1–24:1. Polyesters should be thoroughly

dried prior to extrusion, as with injection molding. The suggested melt temperatures are 240–260°C for PBT, 260–275°C for PET, and 230–260°C for PCTI. These polymers have low melt strength at the processing temperature, and where feasible, the lower end of the melt range should be used. When lowering the melt temperatures of PBT and PET, care should be taken near the melting points (225 and 250°C, respectively) and under shearing conditions, since these polymers may crystallize and resolidify. Molten polyesters should be supported close to the die lips in order to retain the desired configuration. It is a good practice to design the die in a way to minimize melt hang-up which, if severe, could cause degradation and quality problems. The molecular weight requirements of the resins differ according to extrusion applications. Usually low molecular weight polymers are preferred for low tex (den) fibers; PET and PBT of $[\eta]$ 0.6–0.7 and 0.8–0.9 dL/g, respectively, are preferred (160). High molecular weight PET with an $[\eta]$ 1.0 dL/g and higher is employed to make fibers requiring toughness (eg, in tire cords). For films high molecular weight is required so that tears and holes do not occur during extrusion. Excellent films are obtained from PBT with $[\eta]$ 1.2–1.3 dL/g. Biaxially oriented PET films are widely used for their exceptional toughness and tear strength (see POLYESTERS, FILMS).

Quenching PBT from the melt to an amorphous state is exceedingly difficult because of its fast crystallization rate. Thus under all known molding and extrusion conditions, PBT always remains partially crystalline (25–35% minimum, estimated from heats of fusion). Films of PBT are highly transparent and tough when formed in thin sections of ≤ 0.2 mm, using rapid cooling and some shear. The size of crystallites is small enough so that light is not scattered sufficiently to make the film opaque. For thicknesses above 0.2–0.25 mm, larger crystallites and spherulites cannot be avoided, resulting in opaque white extrudates. Chill-roll temperatures of 60–80°C are used to make PBT sheets and films. In order to achieve desired dimensions and uniformity for tubes and pipes, internal air pressure and a vacuum sizing chamber can be used. To cool the tubing, pipe, or profile to a dimensionally stable state rapidly, a water bath at 10–25°C is used. Extrusion of PET into a crystallized state is difficult because of the necessity to maintain the extrudate above 120°C (preferably 140–150°C) for a sufficient time to allow crystallization. High molecular weight ($\bar{M}_w > 40,000$) PET can be extruded into amorphous sheet, pipes, and profiles by use of cold water (10°C) to achieve rapid quenching. Extruded parts are transparent and usable up to the glass-transition temperature (69°C) of PET. Amorphous films and monofilaments can be oriented and heat-set to give strong and tough products (see FILMS, MANUFACTURE).

PCTI does not crystallize and thus only amorphous parts are produced. This polymer has excellent melt strength and easily forms transparent and tough sheeting (qv), pipe (qv), and profiles. The polymer melt can be quenched on chill rolls or in a cooling water bath below the T_g of 80°C, usually at 10–25°C.

In general, high molecular weight TPEs are required for extrusion so that the shape does not change once the part is out of the die. This processing condition can be approached by lowering the processing temperature and minimizing the distance between the melt extrudate and the die. It is also possible to use branched or lightly cross-linked resins that exhibit greater melt strength or elasticity. The generation of branching sites during extrusion is limited by equipment problems,

shear degradation, and the diffusion rate of by-products from the high melt viscosity (161–168). Therefore, solid-state polymerization of intermediate molecular weight material or the use of additives (eg, branching agents), followed by solid-state polymerization described previously, are the preferred methods to increase molecular weights (47,82,169–182). Reactive polymers (eg, ethylene–maleic anhydride copolymers and block copolymers) have been melt-blended with PBT to increase melt strength for extrusion applications (183–187) (see also EXTRUSION).

Blow Molding. This process has become important for bottle forming, principally from PET and PCTL. There are three main blow-molding (BM) techniques: extrusion BM, injection BM, and reheat stretch BM. The latter technique is widely used for bottle-grade PET because of its great number of advantages (188–191). This process provides critical strength to the finished bottle because of biaxial orientation (qv) of the polymer. The molecular orientation enhances clarity, improves impact strength, provides gas- and water-vapor-barrier characteristics, and reduces creep (192,193). Excellent studies have been published on various aspects of blow molding (194–199).

Stretch BM may be an in-line or a two-stage process. In the latter a preform or parison is made in a separate injection-molding operation. This parison is reheated and conditioned at an orientation temperature between the T_g and the melting point, and is then transferred to a BM machine. A rod is inserted into the parison to stretch and orient it axially and to center it in the bottle mold. High pressure air is injected to shape the resin against the walls, thereby providing radial orientation. Rates of 10,000 bottles per h can be achieved in multicavity tools. In the case of the in-line process, parisons are directly transferred from the mold, through the conditioning oven, to the blowing head. The resins are subjected to lower heat treatment, but at the expense of output rate and thread-or-neck-forming precision.

Degradation during polymerization and processing causes formation of acetaldehyde. A newer process called compress-orient BM is claimed to reduce acetaldehyde content, increase wall-thickness control, and lower costs (200). Resin is injected into the mold at low temperature and pressure. A core is inserted to compress the resin and cause it to flow and fill the cavity. From this point the process is similar to the stretch BM used for parisons. These mild molding conditions reduce the acetaldehyde content by 50% because of less thermal degradation of PET. The acetaldehyde content in the final bottle is an important factor. It must be kept below 6 ppm, otherwise it imparts a fruity flavor to the contents of a bottle (201,202). Resins with minimum acetaldehyde content can be prepared by conducting the final stages of the polymerization in the solid state, thereby minimizing thermal degradation and purging acetaldehyde and other volatiles from the resin.

In order to maintain consistent properties and uniform processing from different batches and various resin suppliers, PET is specified for 2-L bottles with an intrinsic viscosity of 0.72 dL/g, corresponding to an \bar{M}_n of ca 24,000. Typically, this is made by melt polycondensation to ca 0.66 dL/g $[\eta]$ followed by solid-state polymerization to the final viscosity. In the case of 1-L and smaller bottles, higher molecular weight resins are preferred with $[\eta]$ of 0.8–1.0 dL/g. The resins having intrinsic viscosities below 0.70 dL/g crystallize too fast, which causes cloudiness and reduced toughness (see also BLOW MOLDING).

Filament, Film, and Sheet. One of the largest uses of TPEs is in monofilament extrusion, eg, for textiles, brush bristles, and tire cords. Films (qv) are extensively used in the packaging and photographic industries. These markets have been dominated by PET, but PBT and copolymers of PET also have been used successfully and have some advantages. Films can be made as a single layer or can be coextruded with other polymers into multilayer laminates, sometimes with as many as 100 layers (see FILMS, MULTILAYER). Transparent film from PBT is achieved by rapid quenching of extruded thin sheet (<0.015 mm). Because of the slow crystallization rate of PET, it can be quenched in air, cold water, or with chill rolls to give clear amorphous sheets with thicknesses of 0.01–0.125 mm. Sheets are transparent and useful up to the T_g of PET. Above T_g crystallization occurs to give cloudy or opaque films. Sheets can be made crystalline by maintaining them at elevated temperature (120–150°C) for sufficient time for crystallization to occur. Biaxial orientation and crystallization of PET film is the most important process to make tough PET film and sheets (see POLYESTERS, FILMS; SHEETING).

Recycling. The rising cost of TPE polymers and their prevalent consumer uses place greater emphasis on scrap and recycling of used resins. The scrap parts from TPEs (eg, sprues and runners) are reground and blended with virgin resin up to 25 wt % for injection molding without significant loss of properties. Scrap can also be used to make parts where optical clarity is not important. The recycling of PET bottles is important due to the huge volume of scrap. Presently in the United States, nine states have bottle-deposit laws, and by 1990, there might be a national bottle-return law. There is a continuing need for efficient, cost-effective recovery and recycling systems that can turn scrap bottles into useful products (203). Recycled PET cannot be used to make more bottles. Most of it goes into low-end products, such as fiberfill for pillows and outerwear, polyester foams, and strapping (204–211). Another new product that competes effectively with other foams is a cushioning material made from reclaimed PET developed in Japan for automotive seats and bedding. A special process converts the scrap into short-fiber, coiled filament, which is mixed with a liquid adhesive and compression-molded into the desired shape. Use of recycled resin for nonbottle applications will free additional virgin resin for projected new bottling uses such as wine and beer.

Three of the principal resin suppliers, DuPont, Goodyear, and Eastman Kodak, have their own recycling systems, and several machinery producers offer both technology and recycling equipment. In one process separation of aluminum caps and high density polyethylene (HDPE) base cups is carried out before bottle grinding; adhesives, residual sugars, and labels are removed later. Another process offers a complete recycling system which decaps, decups, and color-separates on three granulators (one for base cups, one for clear bottles, and one for green bottles). Recently, a process has been developed in which the whole bottle scrap is ground together and then separated afterward. Currently, there are at least 25 companies active in PET reclamation in the United States. One of the newest plants recycles 72 million bottles per year. In this process bottles are granulated, with or without aluminum caps and HDPE bases, and after a series of separation, washing, and drying steps, separate recycle streams of granulated PET and HDPE are produced. Paper labels are removed by an air-lift system and aluminum from

the caps is electrostatically separated. The key process is the HDPE-PET separation, which is reported to be proprietary. After the PET separation, the resins are washed to remove residual glue and other contaminants, and then dried. The impurity content of the PET is reported to be <0.1%, not including moisture. The price of the recycled PET resin is reported to be 45-55 cents per kg compared to 300 cents per kg for originally manufactured products (see also DISPOSAL AND REUSE OF PLASTICS).

Fabrication

The fabrication of TPEs presents few problems, especially for crystalline PET and PBT. These resins have little tendency to stick to tools because of their high melting points. They can be easily sawed, drilled, turned, milled, filed, threaded, tapped, and reamed (138,139,148,150,153,156-159,212,213).

Machining. Ordinary tools for machining steel, nonferrous metals, and in some cases wood may be used for TPEs. Virgin resins can be efficiently machined with high speed steel tools, but for high volume production, particularly with glass-reinforced resins, the use of carbide-tipped tools is recommended. Sharp cutting tools generate continuous chips without difficulty. Reinforced and non-reinforced grades can be machined readily with various milling machines. Even fire-retardant grades produce good surface finishes using turning tools with various shapes and cutting angles. In order to avoid sharp notches and obtain low peak-to-valley heights, turning tools with rounded points are preferred (rad 0.5-2 mm). Clean holes can be drilled using special drills and conventional twist drills for efficient chip removal. Cutting speeds of 60 m/min and feed rates of 0.6 mm/rev are typical. Under these conditions, holes 10-cm deep can be drilled without the need for cooling. Hacksaws, band saws, and circular saws can be used. Saw blades with teeth set in alternate directions, not too close together, have proven best. Clean surfaces can be obtained, even with thick sections. Grinding can be carried out using ordinary commercial grinding wheels and continuous sanding belts. Chrome oxide green is a recommended paste for prepolishing, and final polishing with a fine abrasive may be subsequently done. With deep grind marks, the polished surface, though smooth, may be undulating. Special cooling is usually not needed when grinding TPEs (see MACHINING).

Welding. Tests have shown that nonreinforced PBT can be satisfactorily joined by means of hot gas or heated welding tools. The greater the content of glass fiber and fire retardants is, however, the weaker the resultant weld. When the surfaces to be welded are smooth, friction welding is highly suitable for nonreinforced and reinforced PBT. Electrode pressure and rotational speed are dependent on each other and can easily be determined empirically. Ultrasonic welding produces short welding times and good joint strength with PBT. This technique also facilitates the embedding of metal inserts such as threaded bushes. Essential preconditions for ultrasonic welding are an exact fit between the mating parts and the ability to accomplish the jointing operation without additional mechanical pressure. In some cases, step jointing is recommended because it provides a stronger joint than does butt welding, since the total area of the mating surface is larger.